Supporting Information

Phytic Acid Cross-linked and Hoffmeister effect Strengthened Polyvinyl Alcohol Hydrogels for Zinc Ion Storage

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Experimental

Preparation of hydrogels

The PVA/PA hydrogels were synthesized via simple freeze/thaw process. In detail, 10 wt% transparent PVA solution was firstly prepared by adding PVA (M.W. 105000) into phytic solution (50 wt%) with continuous stirring for 4 h. After transferred to a plastic moule overnight, the sticky solution was stored in a refrigerator at -25 ºC for 2 h and then stand for 2 h at ambient temperature. The above freeze/thaw procedure was repeated three times. Finally, the above hydrogel was immersed into 2.0 M $ZnSO_4$ solution for 2 h to yield PVA/PA flexible hydrogels.

Materials characterizations and electrochemical measurements

The morphologies of all hydrogels were observed by field emission transmission electron microscope (SEM). The crystal structure of MnO_2 nanorods was determined by X-ray diffractometer (XRD) with scanning angle from 5º to 80º. The zinc plate was polished before assembly in coincell. Zn||AC asymmetric or Zn||MnO_2 cells were assembled in CR2032 coin cells with Zn, glass fibers (GF/A), hydrogels electrolyte, and activated carbon or MnO_2 cathode (Aladdin, 99%, metals basis). MnO_2 cathodes or AC electrode were fabricated by pasting 70% MnO_2 or AC, 20% carbon black, and 10% lithium polyacrylate (LiPAA) binder onto Ti foil. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed on a CHI660E electrochemical workstation.

Supporting Figures

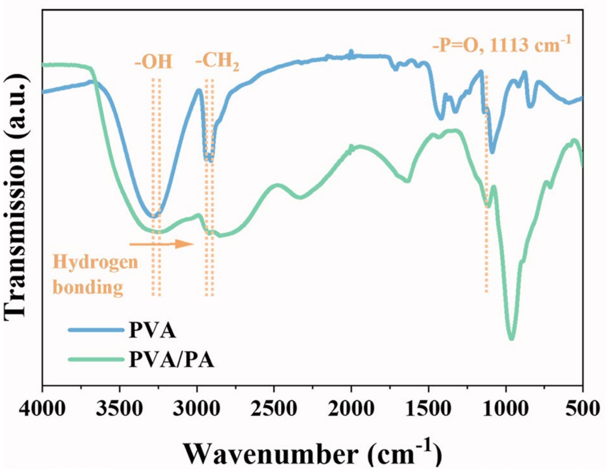

Fig. S1 FT-IR spectra of pure PVA and PVA/PA hydrogels [1-2].

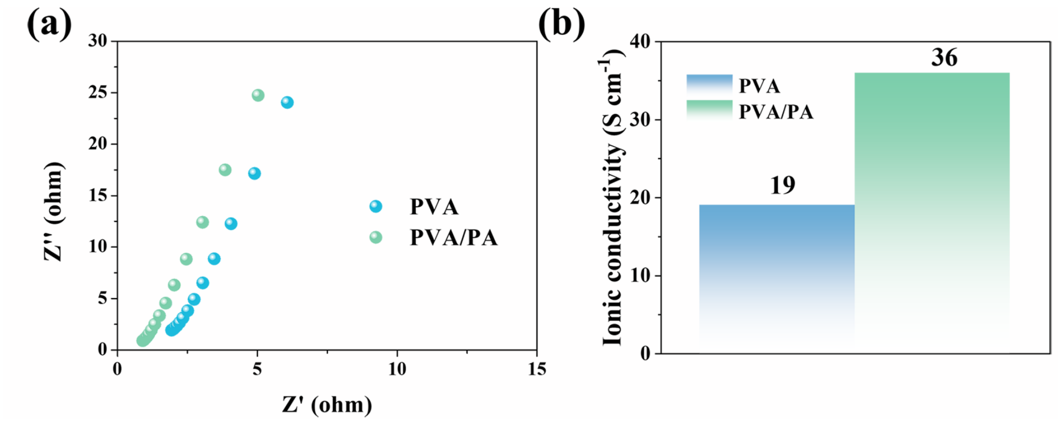

Fig. S2. a) EIS curves of PVA and PVA/PA hydrogels; b) Bar chart of ionic conductivity calculated based on the following formula.

The ionic conductivity σ (S/m) of the hydrogel can be calculated from the EIS curve by the following formula:

$$\sigma = L/(R \times S) \times 100$$

where L (cm) is the distance between the two electrodes, R (Ω) is the bulk resistance, and S (cm^2) is the contact area between the hydrogel and the electrodes. The contact area is controlled at 1.13 cm^{-2}.

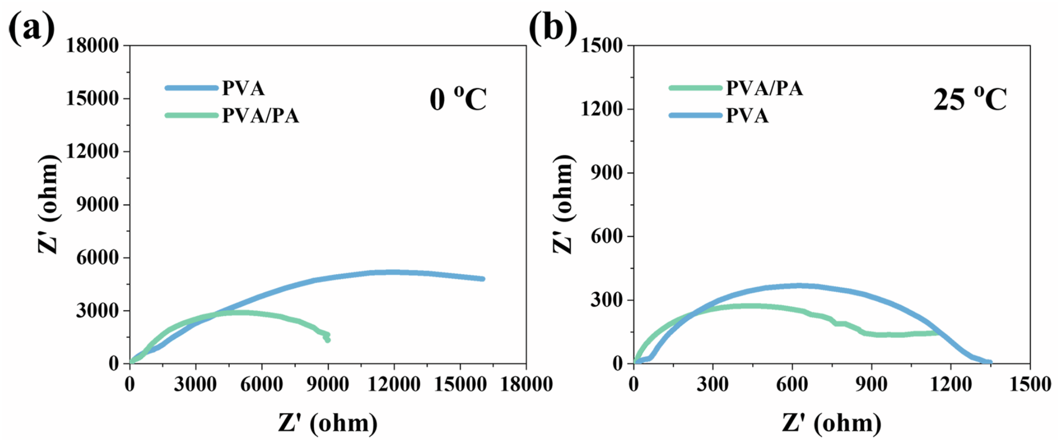

Fig. S3. EIS curves of PVA and PVA/PA hydrogel at room temperature and freezing point.

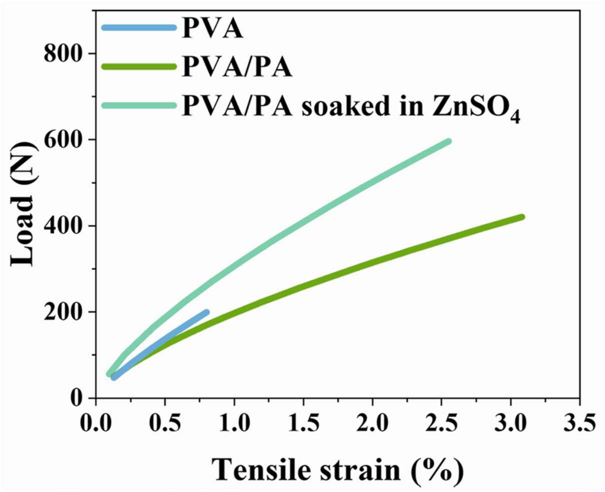

Fig. S4. Tensile strain of PVA, PVA/PA, and soaked PVA/PA hydrogels.

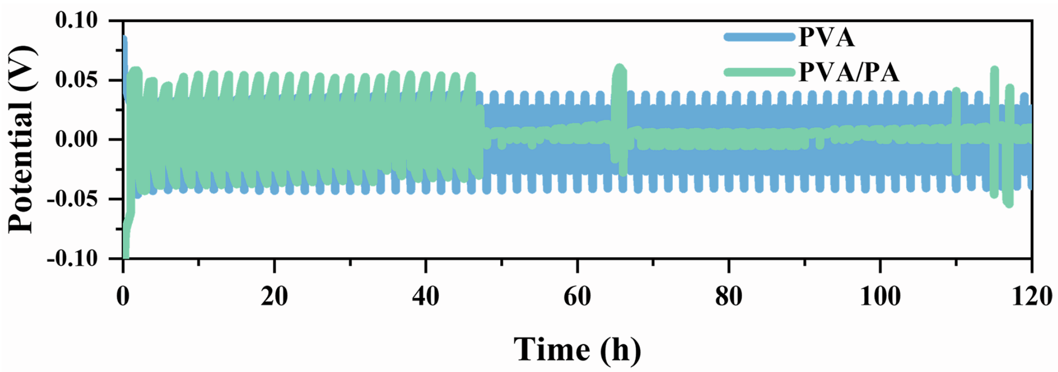

Fig. S5 Time-voltage curve for Zn||Zn cell of hydrogel electrolytes at 1.0 mA cm^{-2}.

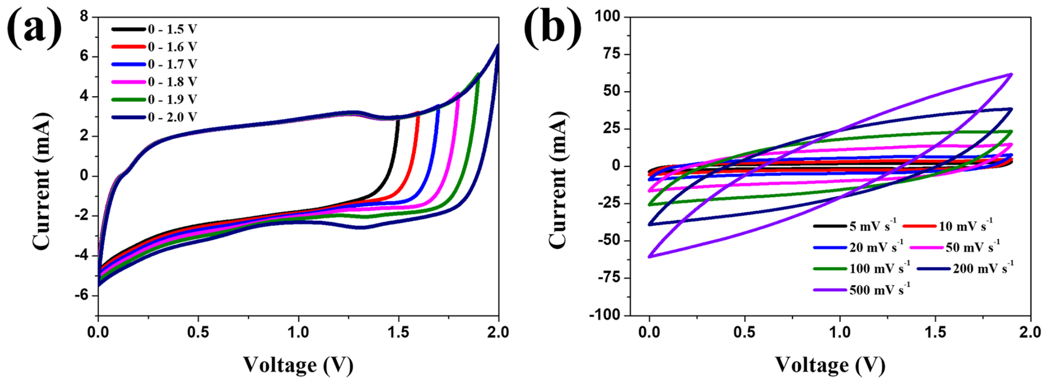

Fig. S6. a) CV curves in Zn|PVA/PA|AC asymmetric capacitor with scanning rate of 5.0 mV s^{-1}; b) CV curves of Zn||AC capacitor at various scan rate.

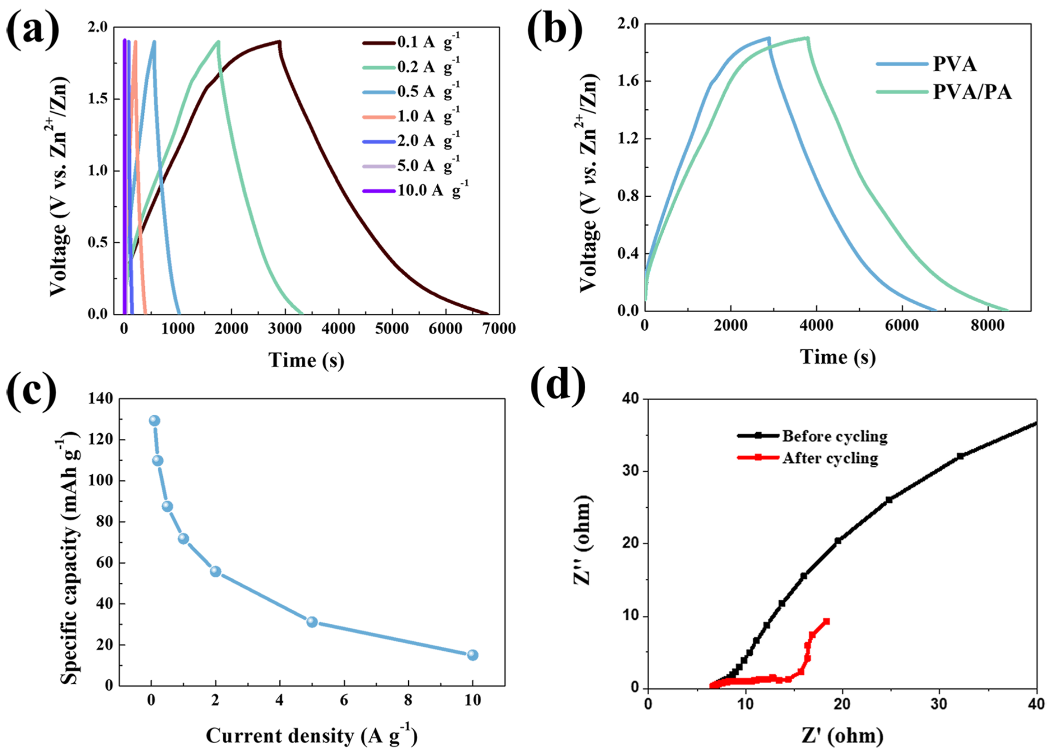

Fig. S7. a) Galvanostatic charge/discharge profiles of PAV hydrogel; b) Comparison of charge/discharge profiles between PVA and PVA/PA hydrogels at 0.1 A g^{-1}; c) Rate capability under different current densities. d) EIS curves of PVA/PA hydrogel before after cycling.

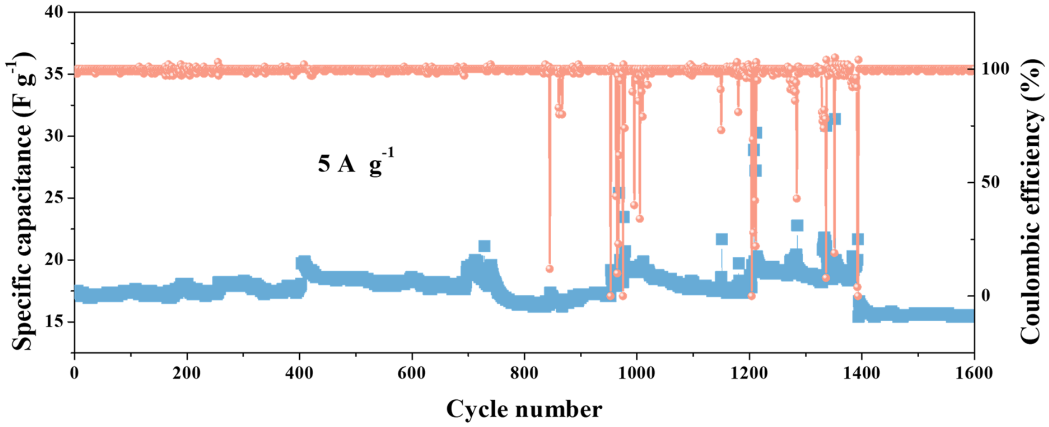

Figure S8. a) Cycling performance at a current density of 5.0 A g^{-1}.

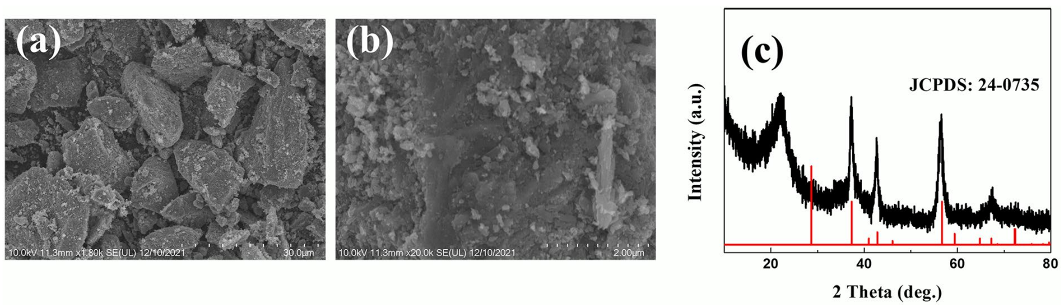

Fig. S9. a,b) SEM images of as synthesized MnO_2 nanoparticles. c) XRD pattern of MnO_2 nanoparticles.

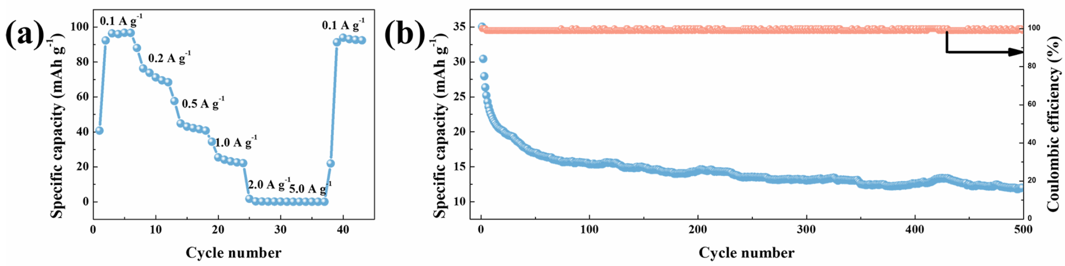

Fig. S10. a) Rate capability and b) cycling performance of PVA hydrogels.

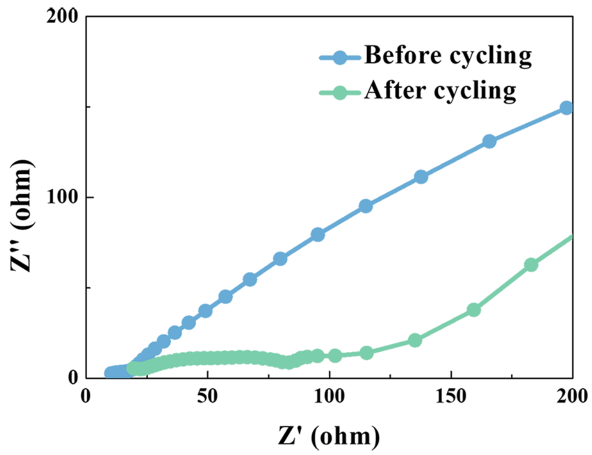

Fig. S11. EIS curve of PVA/PA hydrogels in battery before and after cycling.

Table S1 Full-cell performance of MnO_2 cathodes among reported works.

MnO_2 cathode	Rate capability (A g^{-1}, mAh g^{-1})						
C-MnO_2	0.1	0.2	0.5	1.0	2.0	5.0	This work
	225	200	150	125	100	50	
N doped-MnO_2	0.5	1.0	3.0	5.0	7.0		3
	183.4	128.6	96.4	62.5	50.6		
S doped-MnO_2	0.2	0.5	1.0	2.0			4
	324	311	262	205			
Modified Beta- MnO_2	0.1	0.2	0.3	0.5	0.7	1.0	5
	~225	~200	~183	~160	~145	~105	
Ag doped-MnO_2	0.1	0.2	0.3	0.5	1.0	2.0	6
	290	250	215	177	128	85	
α-MnO_2	0.1	0.15	0.2	0.3	0.5	1.0	7
	~230	~190	~175	~150	~110	~50	
Ag doped-MnO_2	1.0	1.5	2.0	2.5	3.0	3.5	8
	~128	~120	~100	~85	~60	~50	

Supporting References

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